Research Proposal

Proposed Title of Work:ELECTRONIC STRUCTURE AND CHARGE TRANSFER DYNAMICS OF SOME INDIVIDUAL AND COMPOSITE NANOMATERIALS

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ELECTRONIC STRUCTURE AND CHARGE TRANSFER DYNAMICS OF SOME INDIVIDUAL AND COMPOSITE NANOMATERIALS

(a) Origin of the problem:

The efficient, clean, and cost-effective conversion of solar energy into electricity and fuels is one of the most important scientific and technological challenges of this century. In this context, the materials like two dimensional graphene, phosphorene, metal dichlocogenides and their one dimensional nanostructures are of immense inportance because of their tunable electronic and optical properties that can be used in solar cell technology.

To design the next generation solar cell, semiconductor quantum dots (Qds) have also drawn great attention due to their unique physic-chemical properties such as large absorption coefficient, multiple exciton generation, and size-dependent tunablity of their optical and electronc properties which underlie efficient harvesting of solar energy. Recently,perovskite based sensitizers also have attracted great attention due to their superb light-harvesting characteristics. On the basis of the recent achievements, the power conversion efficiency is reported upto 20% which is much greater than the quantum dots sensitized solar cell.

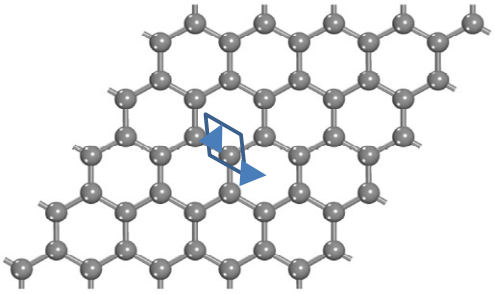
The inorganic-organic nanohybrid systems have been studied extensively from both experimental and theoretical sites as it has been proved that such materials offer greater photovoltaic performance in comparison to the individual counterparts of hybrid system. The main reason behind this is the separation of charge carriers into two different regions of the system thereby lowering the possibility of recombination processes.

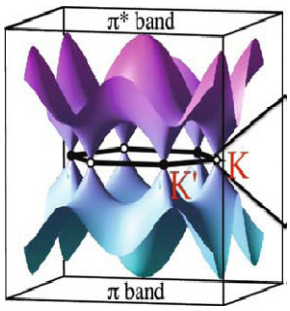
So, there is enormous scope for further developing the materials which may have potential use in optoelectronic devices. The key point is to properly understand the mechanism of charge transfer processes involving the potential energy surfaces of the individual components. Moreover, understanding the dynamics of such processes is in the infancy state. Another big problem is the restriction in system size which can mimic the experimental systems and situations. Approximated DFT based techniques can overcome such barriers and this motivates us to study some individual and composite systems for their exploration in optoelectronic usage.

(b)**Objective of the work:**

Graphene, a one-atom-thick layer of carbon, has charmed materials scientists with its enticing electrical properties that allow electrons to flow freely across its surface. But the material lacks a natural band gap — a range of energy states in which electrons cannot exist freely —

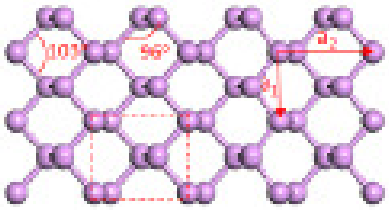
that could be used to switch this flow on and off. This reduces graphene's usefulness as a replacement for the semiconductor switches in computer circuits.[1-4]





Graphene and electronic structure

Recently, two dimension (2D) few-layer black Phosphorus has drawn immediate attention to the socience of material science.This material is chemically inert and has promising transport properties. It has carrier mobility upto 1000 cm^2/Vs and an on/off ratio up to 10^4 was achieved for the phosphorene transistors at room temperature. Phosphorene is an unexploded 2-D semiconductor with a high hole mobility, as a p-type semiconducting materials.[5-8]

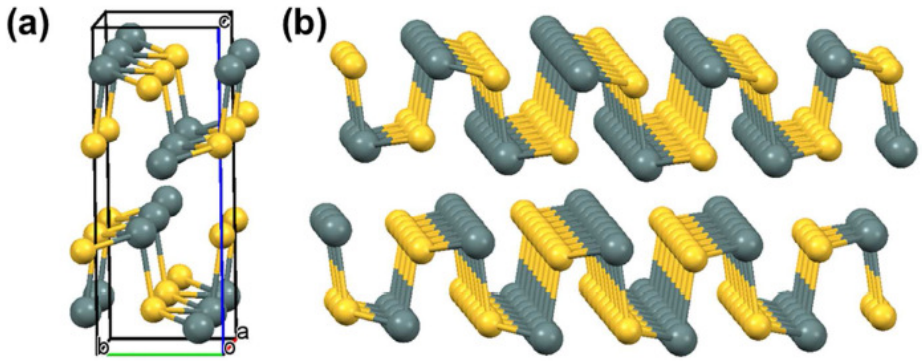


Crystal structure of phosphorene.

However, questions remain the stability of phosphorene with respect to oxidation to phosphoric acids in humid conditions and in the presence of light. The mechanism of degradation still remains unclear and thus unanswered questions loom regarding the future use of the material.

On the other hand, metal dichalcogenides such as MoS_2 have been studied extensively but their low mobilties restrict their applications in electronic devices.[9-1]However, monochalcogenides of group IV such as SnS nanosheets have previously been produced by mainly bottom-up methods.The synthesis of few-layer SnS nanosheets by liquid-phase exfoliation is also well established. Liquid-phase exfoliation to prepare SnS nanosheets from bulk SnS (Herzenbergite) have been discussed. Orthorhombic tin(II) sulfide (SnS, Herzenbergite) is a binary main group chalcogenide that has recently attracted interest because it is a semiconductor. The crystal structure of Herzenbergite is a layered structure of strong Sn-S bonds within a puckered *a-b* sheet with weak intermolecular interactions between the layers that is similar in structure to that of black phosphorus, with which it is isoelectronic. SnS is relatively non-toxic, comprised of earth abundant elements and has an

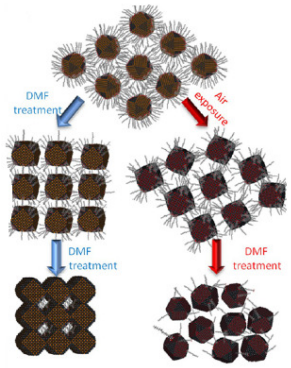
indirect band gap similar in energy to silicon with a large absorbance coefficient ($\alpha > 10^4$) across the ultraviolet, visible and near infrared regions of the electromagnetic spectrum, making it potentially useful for photovoltaic applications.



The crystal structures of the compounds described in this study. (a) The orthorhombic unit cell ofHerzenbergite, tin(II) sulfide (a = 3.98 A; b = 4.33 A; c = 11.18 A; $\alpha = \beta = \gamma = 90°$; space group *P m c n*;Crystallography Open Database ID: 1011253) which generates corrugated layers of SnS held together by weak interlayer forces. (b) A SnS bilayer nanosheet viewed close to the [100] direction i.e. parallel to the sheets.

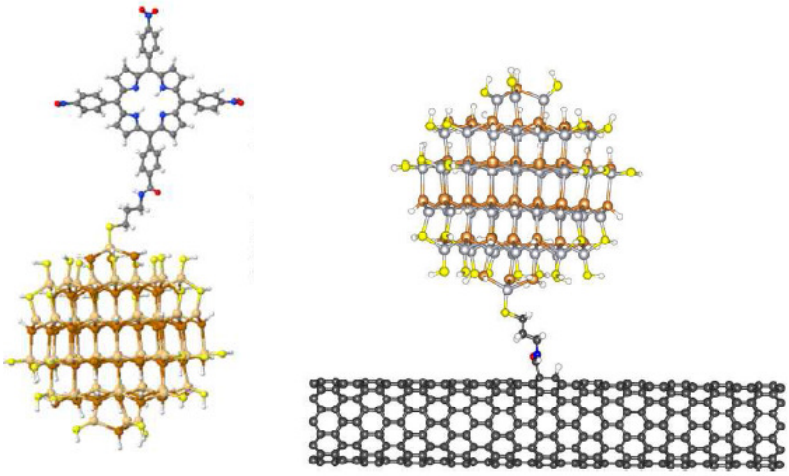
Very recently, SnS nanoribbons have been successfully synthesized with exciting optpelectronic properties. Although SnSNRs are experimentally synthesized but theoretical studies addressing detail structure, stability are still missing. We believe that to forther explore these tin sulphide nanoribbons for different optoelectronic applications the detailed understanding of the electronc structure and its tuning is utmost important.

In contrast to the two dimensional and one dimensional semiconductor, zero dimensional semiconductor quantum dots have drawn great attention due to its more quantum confinement effect. Among the semiconductors quantum dots, cadmium chalcogenides semiconductor nanocrystals is the subject of extensive study because of its diverse application from biologocial labelling to third-generation solar cells.



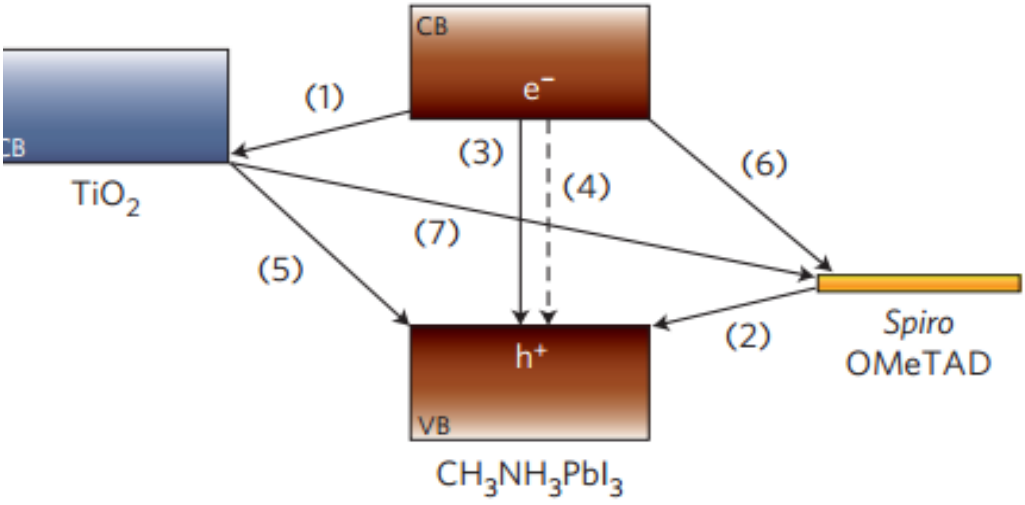
Assembly of PbSe QDs

The inorganic-organic nanohybrids system have been studied extensively, which provide greater photovoltaic performance of hybrid system as compared to individual semiconductor materials.[20-29]



Composite of CdTe QD and porphyrin (left side) and CdTe QD and carbon nanotube (right side)

In recent past, perovskite solar cell have drawn great interest due to its high photovoltaic efficiency.[30]



Electronic dynamics of perovskite

From the above mentioned work, we have interested to study the electronic structure of some individual and composite nanomaterials to optimize the photovoltaic effeciency.The first step static energy calculations will be focused for understanding the energy band alignment and

charge distribution within the isolated or composite nanomaterials. To select the materials for next step dynamical studies we will consider the following points:

i) Electronic energy levels of the individual components and the hybrid systems to understand the band energy alignment. This will provide the value of free energy of electron injection from donor to acceptor moiety.

(ii) Spatial dependence of charge densities of frontier orbitals. This will give us the idea if there is any spatial charge separation in the system that influences the recombination dynamics.

The dynamical studies will bring the information regarding the time scale and hence rates of the concerned processes. Specifically, we seek to investigate the following questions:

a) What factors govern the time-scales and mechanisms of photo-excited electron transfer dynamics?
b) How ligands and size of the nanostructure influence the electron or hole relaxation dynamics?
c) How different is the excited state dynamics in the composite compared to the individual ones?

(c) COMPUTATIONAL METHOD:

The ultimate goal in Solid state Physics is to solve Schrödinger equation-

$\hat{H}\Psi(r;R) = E\Psi(r;R)$ …(1)

Where,

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \quad \ldots(2)$$

Where,

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right),$$

M_A = Mass of nucleus A
Z_A = Atomic number of nucleus A
T_e = Kinetic energy operator for the electron
T_N = Kinetic energy operator for the nuclei
V_{eN}= Operator forpotential energy of the attractions between the electrons and the nuclei
V_{ee}= Potential energy of repulsions between the electrons
V_{NN} = Operator considering potential energy of repulsions between the nuclei A and B

Equation (1) is impossible to solve in practice for the above Hamiltonian due to presence of cross terms r_{iA}, r_{ij}, R_{AB}. Hence approximation is required.

Born-Oppenheimer approximation:

The nuclei are much heavier than electrons (m_{proton}=1836m_e), hence they move much more slowly and can be considered frozen in a single arrangement (molecular conformation). So the electrons can respond almost instantaneouslyto any change in the nuclear position. Thus, the electrons in a molecule are moving in the field of fixed nuclei. So the term T_N can be neglected and the molecular Hamiltonian becomes-

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \cancel{\underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N}} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}}$$

neglected

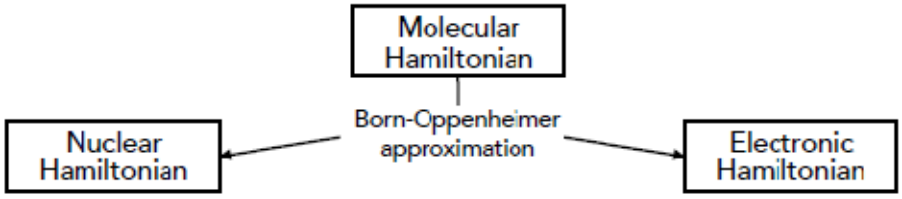
constant term

……(3)

The Born-Oppenheimer approximation allows the total wave function to be written as product of electronic and nuclear wave function as follows

$\Psi(r, R) = \Psi_e(r;R) \bullet \chi_N(R)$

$\Psi_e$is parametrically dependent on position of nucleus(R).



Electronic Hamiltonian describes the motion of N electrons in the field of the M fixed point charges (nuclei).

$$= -\hat{H}_e = \sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}} \qquad \text{……(4)}$$

Electronic Schrödinger equation:

$\hat{H}_e\Psi(r;R) = E_e\Psi(r;R)$ …….(5)

Solution of equation (5) gives the electronic energy E_e and the wave function $\Psi(r;R)$ for a particular value of R.

Finally total energy can be obtained by adding internuclear repulsion energy(V_{NN}) to electronic energy.

Total energy:

$$E_{tot}^{pot}(\mathbf{R}) = E_e + \sum_{A=1}^{M-1} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \quad \ldots\ldots(6)$$

DFTB-NAMD:

Methodologically, DFTB requires set of parameters which should be applicable for a range of pair of elements. The development of such set of parameters is a tricky task. The necessary parameters to represent a system within the DFTB method include the Hamiltonian and overlap matrix elements, Hubbard parameters for every chemical element, and the repulsive pairwise potentials for all interacting neighbors. The successful SCC-DFTB parametrization implies that the main energetic and structural properties are well reproduced with respect to either DFT or the experiment. This can be achieved by adjusting the wave function and density confinement radii for a given element as well as by accurate construction of repulsion profiles. The nonadiabatic couplings and excited states will be obtained using linear-response TD-DFTB, to account for many-body effects. The resulting wavefunctions, excited state forces, and nonadiabatic couplings will be calculated to study nonadiabatic dynamics of excited states.

Time-domain DFTB:

The SCC-DFTB method[1] is implemented within the DFTB+ code.[2] The evolution of single electron KS orbitls $\varphi_p(r, t)$ was determined using time dependent KS equations

$$i\hbar \frac{\partial \varphi(r,t)}{\partial t} = H(\varphi(r, t))\, \varphi_p(r, t), \qquad p = 1, \ldots\ldots, N \qquad \ldots\ldots\ldots\ldots(1)$$

where N is the number of electrons. The equations are coupled, since the Hamiltonian H depends on the density obtained by summing over all the KS orbitals occupied by the N electrons. Expanding the time-dependent KS orbitals

$\varphi_p(r, t)$ in the adiabatic KS orbital basis $\chi_k(r; R)$,

$\varphi_p(r, t) = \sum_{k=1}^{N} c_{pk}(t) \mid \chi_k(r; R) >$, ...(2)

transforms the TDKS equations (1) into the equations for the expansion coefficients

$i\hbar \frac{\delta c_{pk}}{\delta t} = \sum_{m=1}^{N} c_{pm}(t) (\epsilon_m \square_{km} - i\hbar d_{km} . \dot{R})$. .....(3)

The adiabatic KS orbitals, $\chi_k(r; R)$, were obtained with DFTB for atomic positions at each time step along the MD trajectory. The NA coupling describes the electron–phonon interaction

$$d_{km} . \dot{R} = <\chi_k(r; R)| \nabla_R| \chi_k(r; R) > . \dot{R} \quad .....(4)$$

$$= <\chi_k(r; R)| \frac{\partial}{\partial t}| \chi_k(r; R) > \quad .....(5)$$

The NA electron–phonon coupling arises due to the dependence of the adiabatic KS orbitals on the phonon dynamics R(t). Nuclear trajectories from the ground state MD were used to sample initial conditions to create ensemble averages for the NA dynamics.

NAMD simulaton:

Fewest switching surface hopping (FSSH)[3,4] prescribes a probability for hopping between quantum states. Specifically, the probability of a hop from a given state
K to another state m within the time interval dt is

$$dP_{km} = \frac{d}{c} dt \quad .....(6)$$

$d = b_{km}$; $c = a_{kk}$

$b_{km} = -2Re (a_{mk} d_{mk} . \dot{R})$ .....(7)

$a_{mk} = c_m^* c_k$. .....(8)

Here, c_k and c_m are coefficients evolved by (3).

Theory for calculating dephasing time:

The vibrationally-induced dephasing times are computed using the optical response function formalism. The dephasing time is associated with fluctuations of the energy levels due to coupling of electrons and holes to phonons of the semiconductor, vibrations of the ligands, motion of the solvent, etc. The normalized autocorrelation function (ACF) for time-dependent energy E(t) is defined as

$$C(t) = \frac{<\Delta E(t)\Delta E(0)>}{<(\Delta E(0))(\Delta E(0))>} \quad .....(9)$$

where $\Delta E(t) \equiv E(t) - \langle E(t) \rangle$ and the angular brackets denote averaging over a statistical ensemble. The dephasing function is obtained by double integration and exponentiation of the unnormalized ACF,

$$D(t) = \exp\left[\frac{1}{\hbar.\hbar}\int_0^t d\Gamma_1 \int_0^{\Gamma 1} d\Gamma_2 \langle(\Delta E(0))^2\rangle C(\Gamma_2)\right] \quad .....(10)$$

The dephasing times were calculated by fitting the dephasing function by a Gaussian function.

Softwares to be used:

We will perform the electronic structure calculation by density functional theory as implemented in SIESTA, DFTB+, DFTB-NAMD, VASP, Gaussian 09 package.

(d) Future Prospect:

In my Ph. D. Works I shall put emphasis on different nanostructure including two dimensional sheet and one dimensional nanoribbins and nanotubes of different shape and sizes and zero dimensional quantum dots and pervoskite materials and different inorganic-organic hybrid nanocomposites which is to be expected as a good candidates in photovoltaic and electronic and spintronic devices.

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